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THE INTERMOLECULAR POTENTIALS FOR SOME SIMPLE NON-POLAR MOLECULES*

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ABSTRACT

Experimental data on the crystal properties, second virial coefficients, and viscosity coefficients of Ne , A , Kr , Xe , CH_4 , N_2 , CO , O_2 , and CO_2 were analyzed for the purpose of obtaining values of the parameters in the exp-six intermolecular potential, $\varphi(r) = \frac{\epsilon}{1-6/\alpha}\left[\frac{6}{\alpha} e^{\alpha(1-r/r_m)} - \left(\frac{r_m}{r}\right)^6\right]$. For gases whose molecules are spherical, it was possible to reproduce, with a single set of potential parameters, not only the crystal, second virial, and viscosity data, but also data on other transport properties with fair accuracy. For gases whose molecules deviate appreciably from spherical symmetry it was necessary to choose at least two different sets of potential parameters in order to reproduce different types of properties. Such behavior was taken to indicate the inadequacy of the assumptions, made in the fundamental gas theories, that intermolecular forces are central and that intermolecular collisions are elastic.

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Recent calculations of the transport property collision integrals[1] and the second virial coefficients[2] for gases whose molecules obey an exp-six intermolecular potential have enabled the intermolecular potentials of helium and hydrogen to be determined from experimental values of the viscosity and second virial coefficients[3]. The exp-six potential may be written in the form

$$\varphi(r) = \frac{\epsilon}{1-6/\alpha}\left[\frac{6}{\alpha} e^{\alpha(1-r/r_m)} - \left(\frac{r_m}{r}\right)^6\right], \qquad (1)$$

where $\varphi(r)$ is the potential energy of two molecules at a separation distance r, ϵ is the depth of the potential energy minimum, r_m is the position of the minimum, and α is a parameter which is a measure of the steepness of the repulsion energy. Corner[4] has shown how such calculations of intermolecular potentials may be improved by the use of crystal data in addition to gas properties data, and has used this method to determine the potentials of neon and argon from crystal, second virial coefficient, and Joule-Thomson coefficient data. In the present paper we extend the application of Corner's procedure to include experimental transport property results for the evaluation of the intermolecular potentials of a number of simple, non-polar molecules.

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(1) E. A. Mason, J. Chem. Phys. 22, 000 (1954).

(2) W. E. Rice and J. O. Hirschfelder, J. Chem. Phys. 22, 000 (1954).

(3) E. A. Mason and W. E. Rice, J. Chem. Phys. (to be published).

(4) J. Corner, Trans. Faraday Soc. 44, 914 (1948).

DETERMINATION OF POTENTIAL PARAMETERS

The crystal data used in Corner's method are the lattice distance of the crystal, R, and the heat of sublimation, E_o, both at 0^oK. The heat of sublimation is corrected for the zero-point energy by taking it to be the sum of the experimental heat of sublimation at 0^oK (in units of energy/mole) and the quantity $(9N_o k\Theta_D/8)$, where N_o is the Avogadro number, k is the the Boltzmann constant, and Θ_D is the experimental value of the characteristic Debye temperature as determined at low temperatures. Knowledge of the two quantities R and E_o permits the calculation of the two potential parameters r_m and ϵ as a function of the third parameter α by solving the transcendental equation

$$\frac{6C_6}{R^{*7}} - 72(\theta-\theta')e^{\alpha(1-R^*)} + \left(\frac{R^*}{R}\right)\left[\frac{3h^2(\alpha-6)}{8\pi^2 m\epsilon\alpha}\right]^{\frac{1}{2}} X \qquad (2)$$

$$X\left[72\left(\frac{\alpha}{2}-\frac{1}{R^*}\right)e^{\alpha(1-R^*)} - \frac{15C_8}{R^{*8}}\right]^{-\frac{1}{2}}\left[\frac{120C_8}{R^{*9}} + 72\left(\frac{1}{R^{*2}} + \frac{\alpha}{R^*} - \frac{\alpha^2}{2}\right)e^{\alpha(1-R^*)}\right] = 0,$$

where C_6 and C_8 are constants tabulated by Lennard-Jones and Ingham[5], θ and θ' are functions of (αR^*) tabulated by Corner[4], R^* is the reduced lattice distance R/r_m, h is Planck's constant, and m is the mass of one

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(5) J. E. Lennard-Jones and A. E. Ingham, Proc. Roy. Soc. (London) A107, 636 (1925).

molecule. The value of the parameter ϵ appearing in the third term of Eq. (2) is given as a function of α and R* by the equation

$$E_o = \frac{N_o \epsilon}{2(\alpha-6)}\left[\frac{C_6}{R^{*6}} - 72\,\theta\, e^{\alpha(1-R^*)}\right] . \qquad (3)$$

Eqs. (2) and (3) are subject to the conditions that the crystal is cubic and that the zero-point energy is small[6].

The procedure for finding the potential parameters r_m, ϵ, and α is then as follows:

(1) For a chosen arbitrary value of α, the value of R* which satisfies Eq. (2) is found by trial and error. The parameter r_m is found from the relation $r_m = R/R^*$.

(2) The value of ϵ is next calculated directly from Eq. (3).

(3) Another value of α is chosen and the procedure repeated.

A pair of values of r_m and ϵ is thus obtained for each value of α selected.

(4) The value of α is finally found from experimental values of the viscosity and second virial coefficients by the method of translation of axes described in reference (3). In this method a plot of experimental quantities, for example log B(T) vs. log T where B(T) is the second virial coefficient and T is the absolute temperature, is moved until it coincides with one of a family of theoretical curves; the amount of translation parallel to each axis determines r_m and ϵ, and the particular curve chosen from the family

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(6) This condition prevents the use of crystal data in determining the potential parameters of helium and hydrogen.

determines α . In the present case r_m and ϵ are already known for a given α , so the experimental curve is moved the corresponding amount and examined to see if it coincides with the theoretical curve corresponding to the same α as do r_m and ϵ . If not, a new value of α is selected and the process repeated until the values of α coincide.

The above procedure obviously over-specifies the potential parameters; either the viscosity or the second virial coefficient would be sufficient to determine α , whereas we have used both. This fact in itself affords a test of the usefulness of the potential form used, since an unsuitable potential form would be unable to accomplish the simultaneous fit of more than the minimum number of properties needed to evaluate the potential parameters.

Table I lists the potential parameters found by the above procedure for some simple non-polar molecules, and Table II gives a brief summary of the crystal data used to determine the parameters. For comparison, the potential parameters obtained by Corner[4] from crystal, second virial, and Joule-Thomson coefficient data for neon and argon for the Buckingham-Corner potential[7] (which is very similar to the exp-six potential except at small values of the separation distance) are:

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(7) R. A. Buckingham and J. Corner, Proc. Roy. Soc. (London) A189, 118 (1947).

Table I

Exp-six potential parameters for some simple, non-polar molecules.

Substance	Parameters			Exptl. data used for detn. of parameters		
	α	r_m (Å)	ϵ/k °K	Visc.	2nd Virial	Crystal
Ne	14.5	3.147	38.0	a	b	c
A	14.0	3.866	123.2	d	e	c
Kr	12.3	4.056	158.3	f	g	c
Xe	13.0	4.450	231.2	h	i	c
CH_4	14.0	4.206	152.8	j	k	l
N_2	16.2	4.040	113.5	..	m	l
	17.0	4.011	101.2	n	-	-
CO	>17	<4.10	>132	..	o	l
	17.0	3.937	119.1	p	-	-

a. R. S. Edwards, Proc. Roy. Soc. (London) A119, 578 (1928); M. Trautz and H. E. Binkele, Ann. Physik 5, 561 (1930); M. Trautz and R. Zink, ibid. 7, 427 (1930); M. Trautz and H. Zimmerman, ibid. 22, 189 (1935); A. van Itterbeek and O. van Paemel, Physica 7, 265 (1940); R. Wobser and F. Müller, Kolloid-Beihefte 52, 165 (1941); H. L. Johnston and E. R. Grilly, J. Phys. Chem. 46, 948 (1942); van Itterbeek, van Paemel, and van Kierde, Physica 13, 88 (1947); J. W. Buddenberg and C. R. Wilke, J. Phys. Coll. Chem. 55, 1491 (1951).

b. H. K. Onnes and C. A. Crommelin, Leiden Comm. 147d (1915); Crommelin, Martinez, and Onnes, ibid. 154a (1919); L. Holborn and J. Otto, Z. Physik 33, 1 (1925); 38, 359 (1926).

c. G. Kane, J. Chem. Phys. 7, 603 (1939).

d. Y. Ishida, Phys. Rev. 21, 550 (1923); M. Trautz and W. Ludewigs, Ann. Physik 3, 409 (1929); M. Trautz and H. E. Binkele, ibid. 5, 561 (1930); M. Trautz and R. Zink, ibid. 7, 427 (1930); A van Itterbeek and O. van Paemel, Physica 5, 1009 (1938); R. Wobser and F. Müller, Kolloid-Beihefte 52, 165 (1941); H. L. Johnston and E. R. Grilly, J. Phys. Chem. 46, 948 (1942); V. Vasilesco, Ann. Phys. 20, 137, 292 (1945).

e. H. K. Onnes and C. A. Crommelin, Leiden Comm. 118b (1910); L. Holborn and J. Otto, Z. Physik 23, 77 (1924); 33, 1 (1925); Michels, Wijker, and Wijker, Physica 15, 627 (1949).

f. A. O. Rankine, Proc. Roy. Soc. (London) A83, 516 (1910); A84, 181 (1910); A. G. Nasini and C. Rossi, Gazz. Chim. Ital. 58, 433, 898 (1928).

g. Beattie, Brierley, and Barriault, J. Chem. Phys. 20, 1615 (1952).

h. A. O. Rankine, Proc. Roy. Soc. (London) A83, 516 (1910); A84, 181 (1910); A. G. Nasini and C. Rossi, Gazz. Chim. Ital. 58, 433 (1928); M. Trautz and R. Heberling, Ann. Physik 20, 118 (1934).

i. Beattie, Barriault, and Brierley, J. Chem. Phys. 19, 1222 (1951).

j. A. O. Rankine and C. J. Smith, Phil. Mag. 42, 615 (1921); Y. Ishida, Phys. Rev. 21, 550 (1923); G. Jung and H. Schmick, Z. Physik. Chem. B7, 130 (1930); M. Trautz and R. Zink, Ann. Physik 7, 427 (1930); M. Trautz and K. G. Sorg, ibid. 10, 81 (1931); H. L. Johnston and K. E. McCloskey, J. Phys. Chem. 44, 1038 (1940); R. Wobser and F. Müller, Kolloid-Beihefte 52, 165 (1941).

k. F. A. Freeth and T. T. H. Verschoyle, Proc. Roy. Soc. (London) A130, 453 (1931); A. Michels and G. W. Nederbragt, Physica 2, 1000 (1935).

l. Landolt-Bornstein, Physikalisch-Chemische Tabellen; K. Clusius, Z. Physik. Chem. B3, 41 (1929); J. O. Clayton and W. F. Giaque, J. Am. Chem. Soc. 54, 2610 (1932); 55, 4875, 5071 (1933).

m. H. K. Onnes and A. T. van Urk, Leiden Comm. 169d, e (1924); L. Holborn and J. Otto, Z. Physik 10, 367 (1922); 23, 77 (1924); 30, 320 (1924); 33, 1 (1925); Michels, Wouters, and de Boer, Physica 1, 587 (1934).

n. C. J. Smith, Proc. Phys. Soc. (London) 34, 155 (1922); M. Trautz and P. B. Baumann, Ann. Physik 2, 733 (1929); M. Trautz and W. Ludewigs, ibid. 3, 409 (1929); M. Trautz and A. Melster, ibid. 7, 409 (1930); M. Trautz and R. Zink, ibid. 7, 427 (1930); M. Trautz and R. Heberling, ibid. 10, 155 (1931); M. Trautz and E. Gabriel, ibid. 11, 606 (1931); A. van Itterbeek and W. H. Keesom, Physica 2, 97 (1935); P. J. Rigden, Phil. Mag. 25, 961 (1938);

n. (continued) H. L. Johnston and K. E. McCloskey, J. Phys. Chem. 44, 1038 (1940); R. Wobser and M. Müller, Kolloid-Beihefte 52, 165 (1941); V. Vasilesco, Ann. Phys. 20, 137, 292 (1945); van Itterbeek, van Paemel, and van Lierde, Physica 13, 88 (1947).

o. T. T. H. Verschoyle, Proc. Roy. Soc. (London) A111, 552 (1926); G. A. Scott, ibid. A125, 330 (1929); D. T. A. Townend and L. A. Bhatt, ibid. A134, 502 (1931); Michels, Lupton, Wassenaar, and de Graaf, Physica 18, 121 (1952).

p. C. J. Smith, Proc. Phys. Soc. (London) 34, 155 (1922); M. Trautz and P. B. Baumann, Ann. Physik 2, 733 (1929); M. Trautz and W. Ludewigs, ibid. 3, 409 (1929); M. Trautz and A. Melster, ibid. 7, 409 (1930); R. Wobser and F. Müller, Kolloid-Beihefte 52, 165 (1941); H. L. Johnston and E. R. Grilly, J. Phys. Chem. 46, 948 (1942); van Itterbeek, van Paemel, and van Lierde, Physica 13, 88 (1947).

TABLE II

Summary of crystal data used for the determination of potential parameters.

Substance	R (Å)	E_o (cal./mole)	Θ_D (°K)
Ne	3.10	591	64
A	3.81	2029	80
Kr	3.94	2719	63
Xe	4.33	3901	55
CH_4	4.16	2508	78
N_2	4.02	1804	68
CO	4.08	2083	79.5

Ne: $\alpha = 13.6$, $r_m = 3.16$ Å, $\epsilon/k = 37.1\ ^oK$;

A: $\alpha = 13.9$, $r_m = 3.87$ Å, $\epsilon/k = 123.2\ ^oK$.

The agreement with the exp-six parameters of Table I is satisfactory.

In some cases it was not possible to fit all measured properties with only one set of potential parameters; this failure is discussed in the next section. It was necessary to extrapolate the tables in references (1) and (2); the supplementary tables obtained by the extrapolations are given in the appendix.

COMPARISON WITH EXPERIMENT

A. Spherical Molecules

Included in the category of spherical molecules are neon, argon, krypton, xenon, and methane. Strictly speaking, the theories which relate the second virial coefficients and transport properties to the intermolecular potential are not really applicable to the methane molecule, which has internal degrees of freedom. However, the internal degrees of freedom do not seem to have much effect except in the case of the thermal conductivity, for which the theory fails.

The test of the suitability of Eq. (1) as a potential form is its ability to reproduce gas properties data, since the crystal data are automatically reproduced by the procedure used to determine the potential parameters. Fig. 1 shows a comparison of measured values of the second virial coefficient, B(T), and values calculated from the parameters of Table I according to the

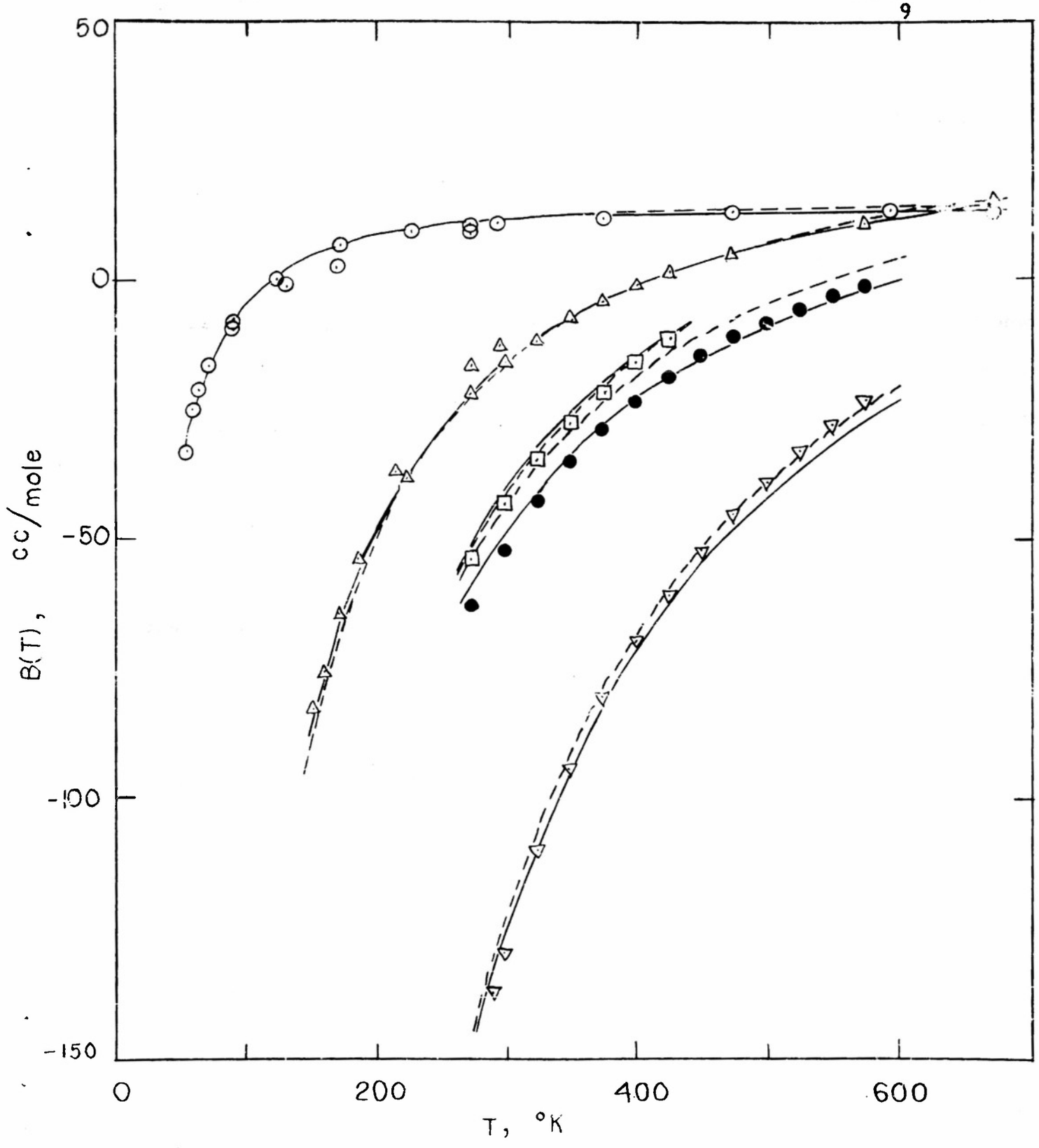

Fig. 1. Comparison of observed and calculated values of the second virial coefficients of spherical molecules. Solid line: exp-six potential; broken line: Lennard-Jones (12-6) potential. Observed values: ⊙ neon, △ argon, ● krypton, ▽ xenon, ⊡ methane.

equations

$$B(T) = b_m B^*(\alpha, T^*) , \tag{4}$$

$$b_m = (2\pi/3) N_o r_m^3 , \tag{5}$$

where $B^*(\alpha, T^*)$ is a dimensionless quantity tabulated in reference (2) as a function of α and T^* $(= kT/\epsilon)$, and the other factors are as previously defined. Also shown are the values of $B(T)$ calculated for the widely used Lennard-Jones (12-6) potential[8]

$$\varphi(r) = \epsilon\left[\left(\frac{r_m}{r}\right)^{12} - 2\left(\frac{r_m}{r}\right)^{6}\right] , \tag{6}$$

where $\varphi(r)$, ϵ, and r_m are defined in connection with Eq. (1). Different values of the parameters r_m and ϵ of the L. J. (12-6) potential are often available for the same substance, depending on which properties were used to evaluate the parameters. We have chosen the values based, at least in part, on crystal data; these are listed in Table III. The agreement between the observed and calculated values of $B(T)$ is excellent in the cases of neon and argon for both the exp-six and the L.J. (12-6) potentials. The agreement is only fair for methane and xenon; for xenon the exp-six potential fits $B(T)$ better at low temperatures, whereas the L. J. (12-6) potential fits better at high temperatures. The agreement in the case of krypton is good for the exp-six

(8) All tabulations necessary for calculating properties of gases obeying a Lennard-Jones (12-6) potential may be found in Hirschfelder, Curtiss, and Bird, The Molecular Theory of Gases and Liquids (John Wiley and Sons, New York, 1954).

TABLE III

Lennard-Jones (12-6) potential parameters for spherical, non-polar molecules.

Substance	Parameters		Ref.
	r_m (Å)	ϵ/k (°K)	
Ne	3.16	36.3	a
A	3.87	119.3	a
Kr	4.04	159	b
Xe	4.46	228	b
CH_4	4.22	148	b

a. "Best" values calculated from crystal and second virial coefficient data by J. Corner (reference (4)).

b. Calculated from crystal data by the method given by J. Corner in Trans. Faraday Soc. 35, 711 (1939).

potential, but rather poor for the L. J. (12-6) potential. On the whole, however, neither potential is markedly superior to the other as judged on the basis of second virial coefficients.

Fig. 2 shows a similar comparison between the experimental values of the viscosity and those calculated from the exp-six parameters of Table I according to the equation

$$10^{7}\eta = \frac{266.93\,(MT)^{\frac{1}{2}}}{r_m^2}\;\frac{f_\eta^{(3)}(\alpha, T^*)}{\Omega^{(2,2)*}(\alpha, T^*)} \qquad (7)$$

where η is the viscosity in gm-cm^{-1}-sec^{-1}, M is the molecular weight, r_m is in angstroms, and $f_\eta^{(3)}(\alpha, T^*)$ and $\Omega^{(2,2)*}(\alpha, T^*)$ are dimensionless functions which may be obtained from the tabulations in reference (1). Also shown are the values calculated from the L. J. (12-6) parameters of Table III. All the experimental values were corrected to a uniform relative basis in which the viscosity of air at 23°C was taken as 1833.0 x 10^{-7} gm-cm^{-1}-sec^{-1}. Several discrepancies between experiment and theory are apparent. The measured values for argon deviate badly from the calculated curves at high temperatures. In this region forces of repulsion dominate, and the slope of the experimental curve implies an extremely steep repulsion energy at close distances of approach of two molecules. However, experiments on the scattering of high velocity argon beams in argon gas[9] give information on the intermolecular

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(9) I. Amdur and E. A. Mason, J. Chem. Phys. (to be published).

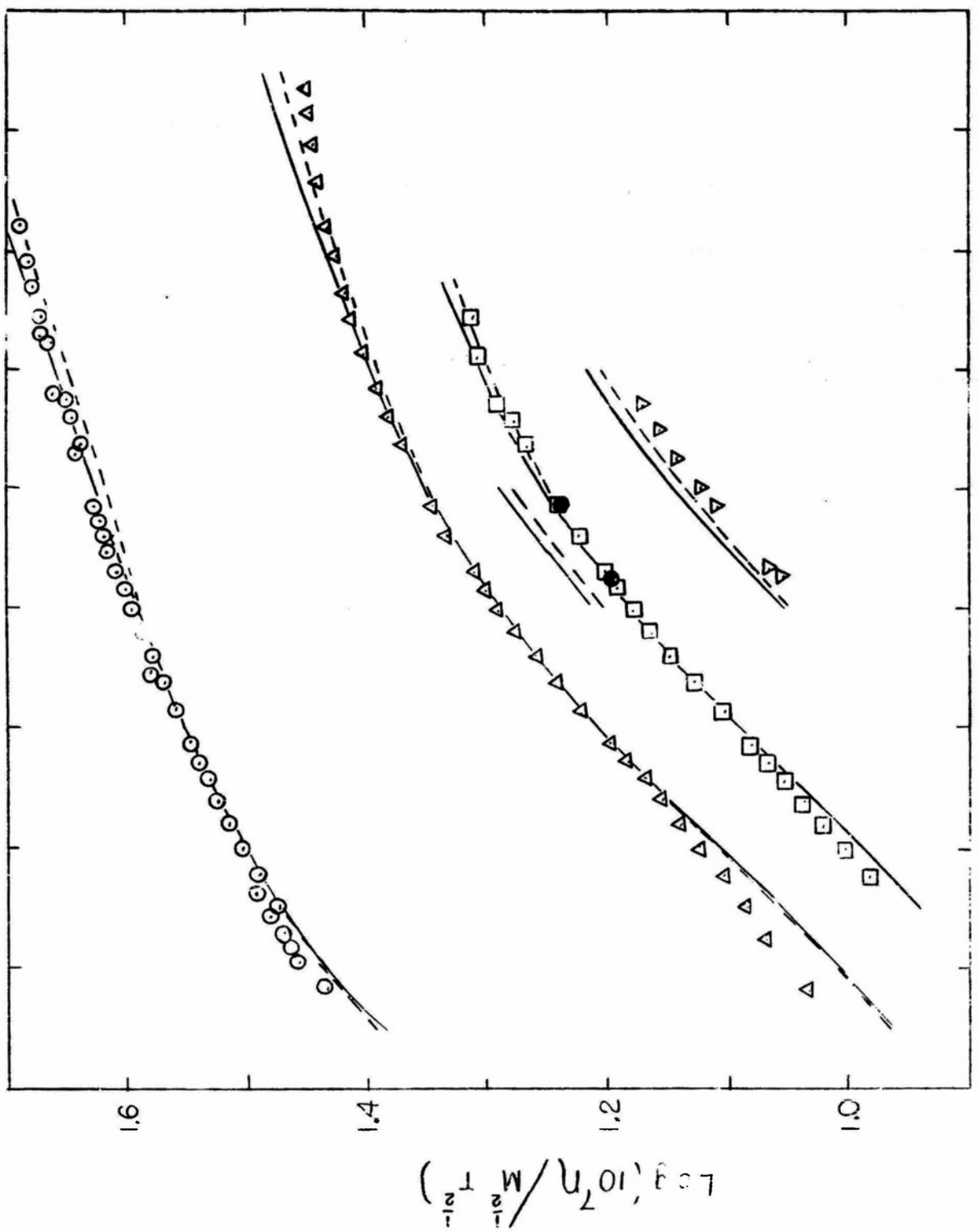

Fig. 2. Comparison of observed and calculated values of the viscosities of spherical molecules. Solid line: exp-six potential; broken line: Lennard-Jones (12-6) potential. Observed values: ⊙ neon, △ argon, ● krypton, ▽ xenon, ⊡ methane.

potential in this region of strong repulsion, and no indication of such a steep repulsion is found. It, therefore, seems likely that the experimental viscosity results for argon are low at high temperatures. The deviations at low temperatures for argon and methane are greater than the estimated experimental error; we can think of no explanation for this. The rather scanty measurements of the viscosities of krypton and xenon are also seen to deviate from the theoretical curves. Since these gases are difficult to obtain pure, it is possible that some light gas impurities were present. Further experiments would be helpful in clarifying this point. Within the experimental error, the exp-six and the L. J. (12-6) potentials are about equally successful in reproducing the experimental viscosities.

A more important test of an intermolecular potential function is its ability to reproduce properties other than the ones used in determining the potential parameters. Fig. 3 shows a comparison between the experimental values[10] of the thermal conductivity and those calculated from the exp-six

(10) A. Eucken, Physik. Zeit. 12, 1101 (1911) (A); S. Weber, Ann. Physik 54, 437, 481 (1917)(Ne , A), Leiden Comm. Suppl. 42b (1919) (Ne); M. Curie and A. Lepape, Compt. Rend. 193, 842 (1931), J. Phys. et Rad. 2, 393 (1931) (Ne, A, Kr, Xe); B. G. Dickens, Proc. Roy. Soc. (London) A143, 517 (1934) (A); W. G. Kannuluik and L. H. Martin, Proc. Roy. Soc. (London) A144, 496 (1934) (Ne, A); W. G. Kannuluik and E. H. Carman, Proc. Phys. Soc. (London) B65, 701 (1952) (Ne, A, Kr, Xe); F. G. Keyes, Project Squid Tech. Mem. MIT-1 (Oct. 1, 1952) (A).

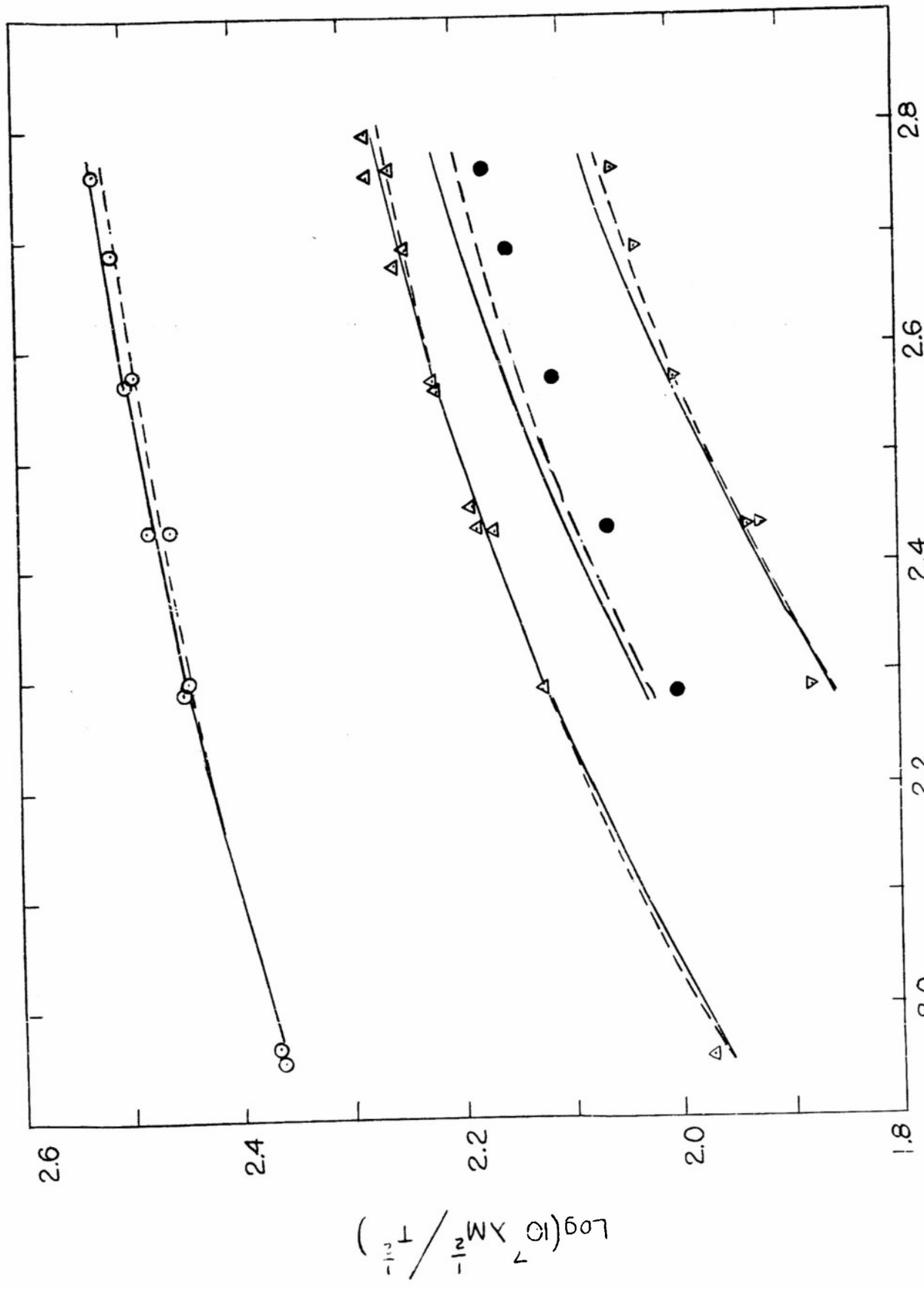

Fig. 3. Comparison of observed and calculated values of the thermal conductivities of spherical molecules. Solid line: exp-six potential; broken line: Lennard-Jones (12-6) potential. Observed values: ⊙ neon, △ argon, ● krypton, ▽ xenon.

parameters of Table I according to the equation

$$10^7 \lambda = \frac{1989.1\ T^{\frac{1}{2}}}{M^{\frac{1}{2}} r_m^2} \frac{f_\lambda^{(3)}(\alpha, T^*)}{\Omega^{(2,2)*}(\alpha, T^*)} , \qquad (8)$$

where λ is the thermal conductivity in cal-cm^{-1}-sec^{-1}-deg^{-1}, $f_\lambda^{(3)}(\alpha, T^*)$ is a dimensionless function tabulated in reference (1), and the other terms are as defined in connection with Eq. (7). Also shown in Fig. 3 are the values of λ calculated for the L. J. (12-6) potential. The theory from which Eq. (8) is derived takes no account of energy transported in the molecular internal degrees of freedom, so methane is excluded from this comparison. No exact method for calculating the transport of energy by the internal degrees of freedom has yet been worked out.

Experimental values of λ are much more difficult to determine accurately than values of η, but within the experimental error the exp-six and L. J. (12-6) potentials reproduce the measured values of λ about equally well. The agreement is excellent for neon and argon, only fair for xenon, and poor for krypton. It should be pointed out that according to Eqs. (7) and (8) values of λ and η for the same gas are not independent, but instead are directly proportional (except for the functions $f_\lambda^{(3)}$ and $f_\eta^{(3)}$, which are very nearly equal). Thus comparison of observed and calculated values of λ is not an independent test of the suitability of potential parameters derived from observed values of η, but is more a check on the consistency of the measured values of λ and η according to the fundamental theory from which Eqs. (7) and (8) are derived. Comparison of Figs. 2 and 3 shows that such measurements are not always

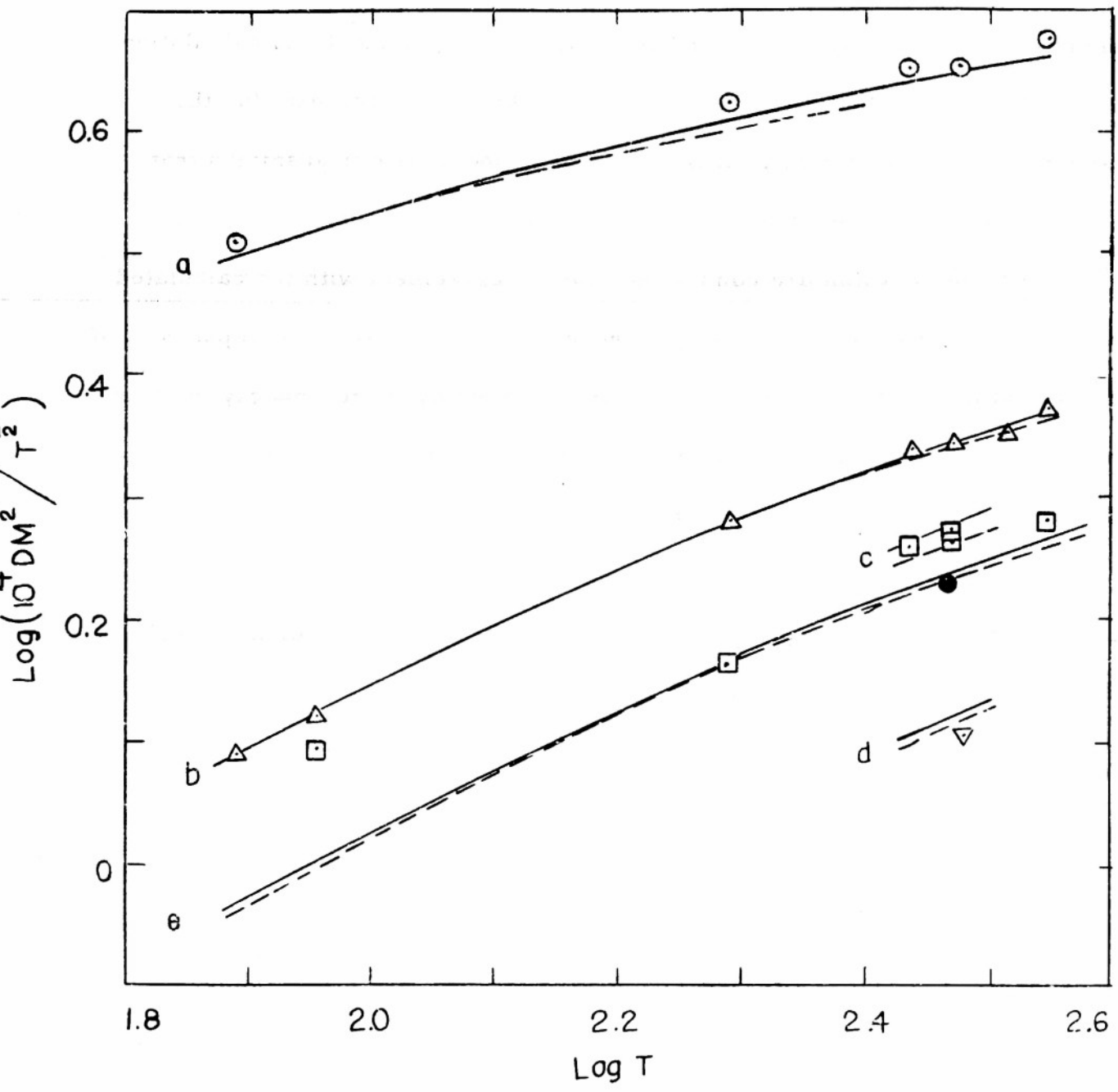

Fig. 4. Comparison observed and calculated values of the self-diffusion coefficients of spherical molecules. Solid line: exp-six potential; broken line: Lennard-Jones (12-6) potential. Observed values: ⊙ neon, △ argon, ● krypton, ▽ xenon, ⊡ methane. Curves a, b, c, d, and e represent neon, argon, krypton, xenon, and methane, respectively.

calculated for the exp-six potential and the L. J. (12-6) potential. The agreement is excellent for argon, fair for neon, and rather poor for krypton, xenon, and methane, for which the scatter of the experimental points is large. Within the scatter of the observed values, both potentials are about equally satisfactory.

A final quantity suitable as a test of potential parameters is the thermal diffusion ratio, k_T. For a binary mixture of heavy isotopes, the m-th approximation to the thermal diffusion ratio, $\left[k_T\right]_m$, may be written as

$$\left[k_T\right]_m = \left[k_T^*\right]_m \left(\frac{M_1 - M_2}{M_1 + M_2}\right) x_1 x_2 , \qquad (10)$$

correct to the first order of the small quantity $(M_1-M_2)/(M_1+M_2)$, where M_1 and M_2 are the molecular weights of the two isotopes, and x_1 and x_2 are their mole fractions in the mixture. The quantity $\left[k_T^*\right]_m$ is a reduced thermal diffusion ratio, and is tabulated in reference (1) for the exp-six potential as a function of α and T^* for $m = 2$. A similar function, designated as R_T, is tabulated for the L. J. (12-6) potential to a first approximation in reference (8); the relation between k_T^* and R_T is: $\left[k_T^*\right]_1 = (105/118)R_T$. Experimental values of k_T^* have been obtained[12] for neon, argon, and methane by measurement of the thermal separation of isotopic mixtures between two absolute temperatures, T and T'. An experimental value of k_T^* is thus a

(12) A. O. Nier, Phys. Rev. 56, 1009 (1939) (CH_4), Phys. Rev. 57, 338 (1940) (Ne); L. G. Stier, Phys. Rev. 62, 548 (1942) (Ne, A); A. K. Mann, Phys. Rev. 73, 413 (1948) (Ne, A); A. N. Davenport and E. R. S. Winter, Trans. Faraday Soc. 47, 1160 (1951) (CH_4).

mean value over the temperature range of T to T', but it may be shown[13] that such a mean value is equal to the actual value at an intermediate temperature, $\bar{T}$, given by

$$\bar{T} = \frac{TT'}{T' - T} \ln (T'/T) \quad . \tag{11}$$

Fig. 5 is a comparison of the experimental and calculated values of the reduced thermal diffusion ratio, k_T^*, as a function of $\bar{T}$. The agreement for argon and methane is slightly better for the exp-six potential than for the L. J. (12-6) potential; for neon the agreement is poor for both potentials. The continued increase of k_T^* for neon at high temperatures implies a very steep repulsive potential[14]; the existence of such a steep repulsion is supported neither by the viscosity data shown in Fig. 2 nor by results obtained from scattering of beams of high velocity neon atoms by neon gas[9]. Further measurements of k_T^* for neon at high temperatures would seem to be desirable.

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(13) H. Brown, Phys. Rev. 58, 661 (1940). See also A. N. Davenport and E. R. S. Winter, Trans. Faraday Soc. 47, 1160 (1951).

(14) T. Kihara, University of Wisconsin Naval Research Laboratory Report WIS-OOR-7, June 5, 1953 (to be published in Rev. Mod. Phys.).

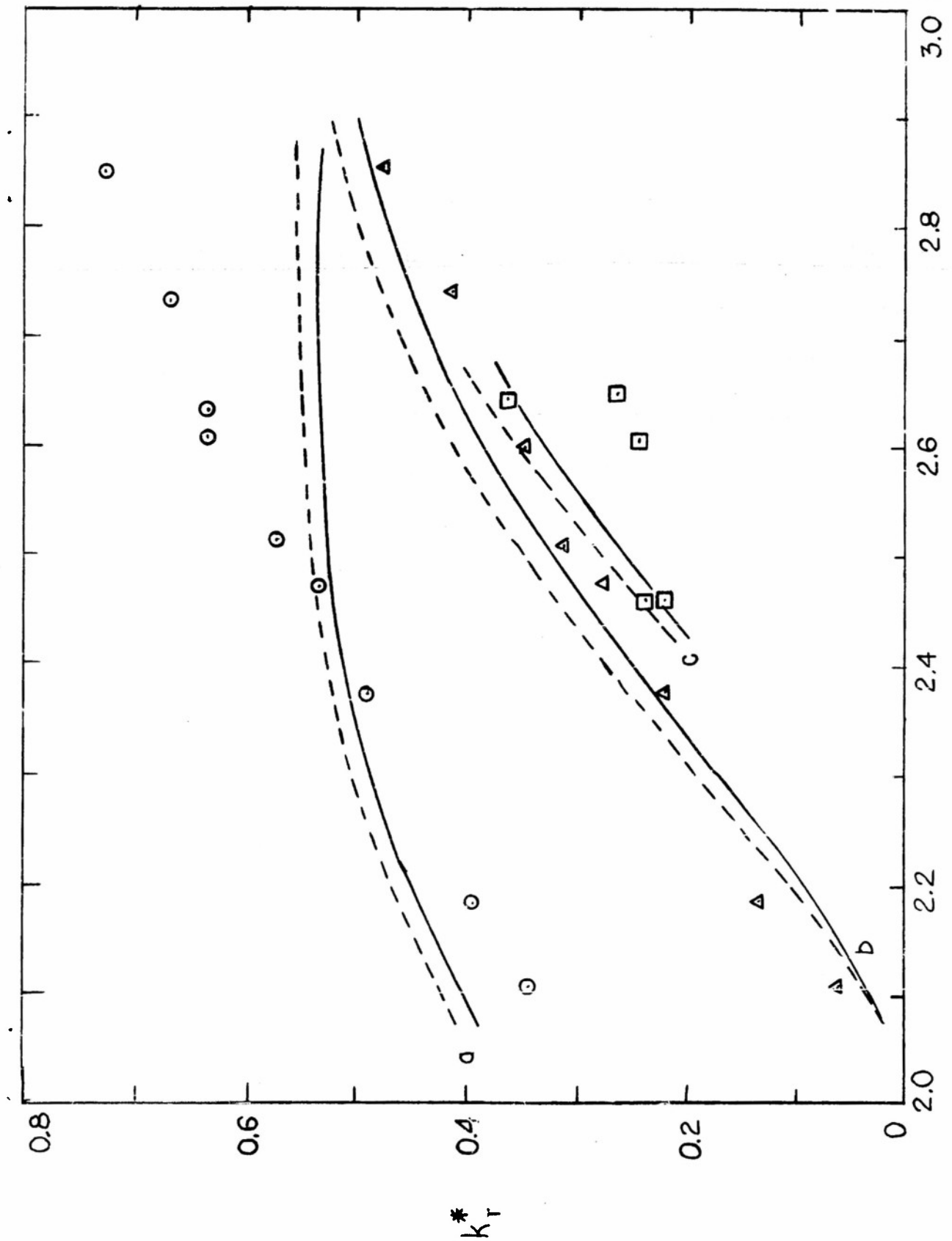

Fig. 5. Comparison of observed and calculated values of the reduced thermal diffusion ratios for spherical molecules. Solid line: exp-six potential; broken line: Lennard-Jones (12-6) potential. Observed values: ⊙ neon, △ argon, ⊡ methane. Curves a, b, and c represent neon, argon, and methane, respectively.

B. Non-Spherical Molecules

Included in this category are nitrogen, carbon monoxide, oxygen, and carbon dioxide. There are of course many other non-spherical, non-polar molecules, but only for these four does there exist a sufficient quantity of experimental data to justify the assignment of three disposable parameters (α , r_m , ϵ) on the basis of the measured properties.

The L. J. (12-6) potential has not been completely successful in reproducing the measured properties of gases composed of non-spherical molecules, the principal difficulty being that different potential parameters are required to fit different properties of the same substance. The question arises whether the fault is primarily that the potential form is inadequate, or that the basic theory is inapplicable because of its assumptions of spherically symmetric intermolecular potentials and elastic intermolecular collisions. Some light might be thrown on this question by the use of the exp-six potential, which is more realistic and contains more disposable parameters than the L. J. (12-6) potential. If the exp-six potential fails for non-spherical molecules in the same way as does the L. J. (12-6), it might reasonably be supposed that the trouble lies primarily with the basic theory rather than with the potential form.

It is not necessary to look far to see that the exp-six potential is not entirely successful in dealing with non-spherical molecules. Oxygen and carbon dioxide cannot be handled by the method used for spherical molecules because they do not crystallize in the cubic form. Clearly the non-spherical nature of the molecule has a strong effect on the crystal properties, but it is

not even possible to fit both the second virial and the viscosity coefficients of oxygen and carbon dioxide with a single set of potential parameters. The best that can be done is to assign different parameters for each property, thereby reducing the exp-six potential to the status of an unnecessarily complicated interpolation function.

The situation is somewhat better for nitrogen and carbon monoxide, which crystallize in the cubic system. Now it is possible to fit both the crystal properties and the second virial coefficients with a single set of potential parameters, but impossible to fit both the crystal properties and the viscosities for any reasonable value of the parameter α. This behavior is shown by our assignment of two sets of potential parameters for nitrogen and carbon monoxide in Table I. The situation is more clearly illustrated in Figs. 6 and 7, where the experimental second virial and viscosity coefficients of nitrogen are compared with the values calculated from the two sets of parameters in Table I. Each set of parameters accurately reproduces the experimental results for which the parameters were evaluated, but fails to fit the other experimental results.

Although the exp-six parameters derived from viscosity do not reproduce the crystal properties and second virial coefficients for non-spherical molecules, they may be fairly successful in reproducing other transport properties, as is illustrated in Figs. 8 and 9, where experimental self-diffusion coefficients[15] and thermal diffusion ratios[16] of nitrogen are compared with the values

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(15) E. B. Winn, Phys. Rev. 74, 698 (1948); 80, 1024 (1950); E. R. S. Winter, Trans. Faraday Soc. 47, 342 (1951).

(16) A. K. Mann, Phys. Rev. 73, 413 (1948); A. N. Davenport and E. R. S. Winter, Trans. Faraday Soc. 47, 1160 (1951).

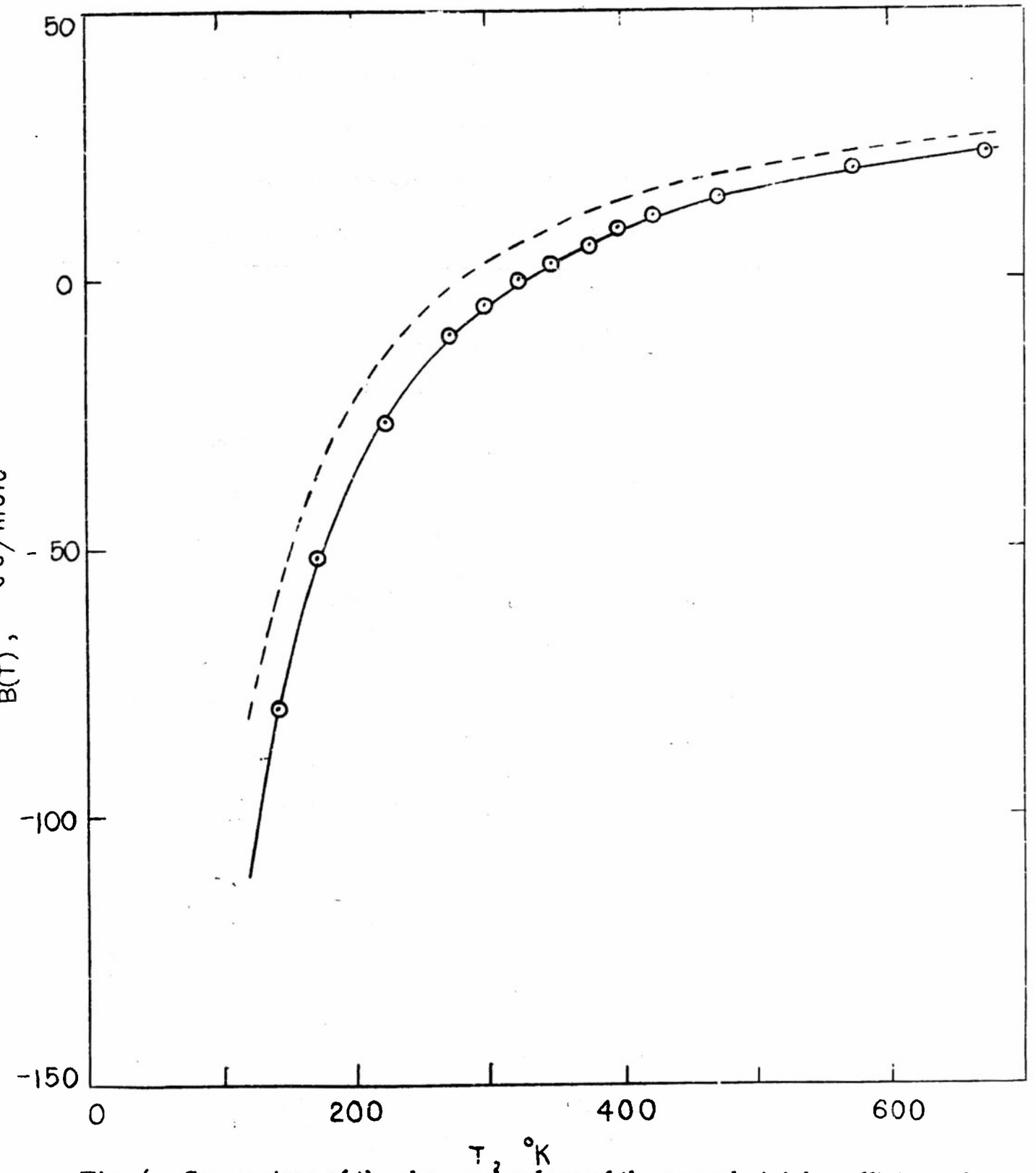

Fig. 6. Comparison of the observed values of the second virial coefficient of nitrogen with the values calculated for the exp-six potential. Solid line: calculated using the parameters derived from crystal properties and second virial coefficients; broken line: calculated using the parameters derived from viscosity.

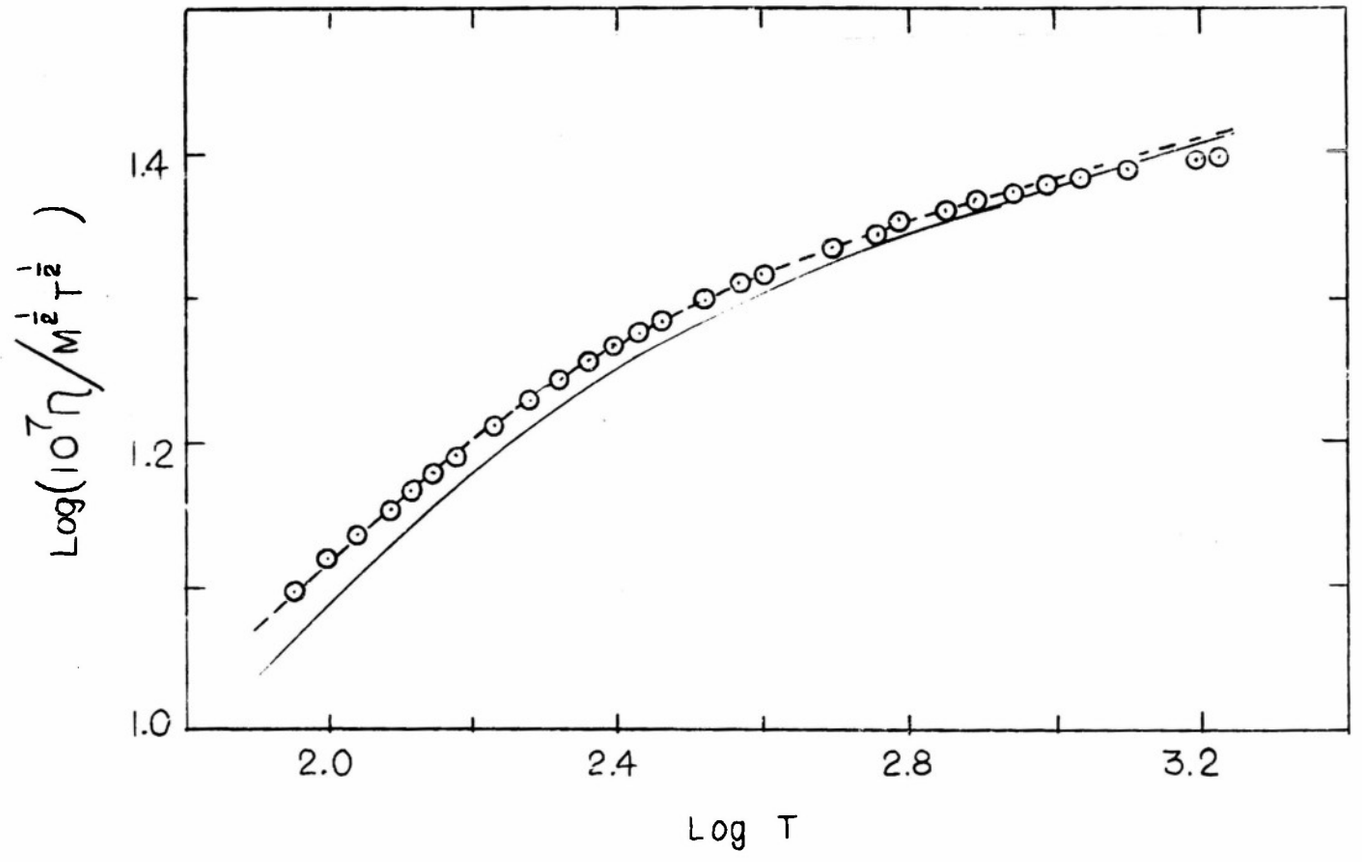

Fig. 7. Comparison of the observed viscosities of nitrogen with those calculated for the exp-six potential. Solid line: calculated using the parameters derived from crystal properties and second virial coefficients; broken line: calculated using the parameters derived from viscosity.

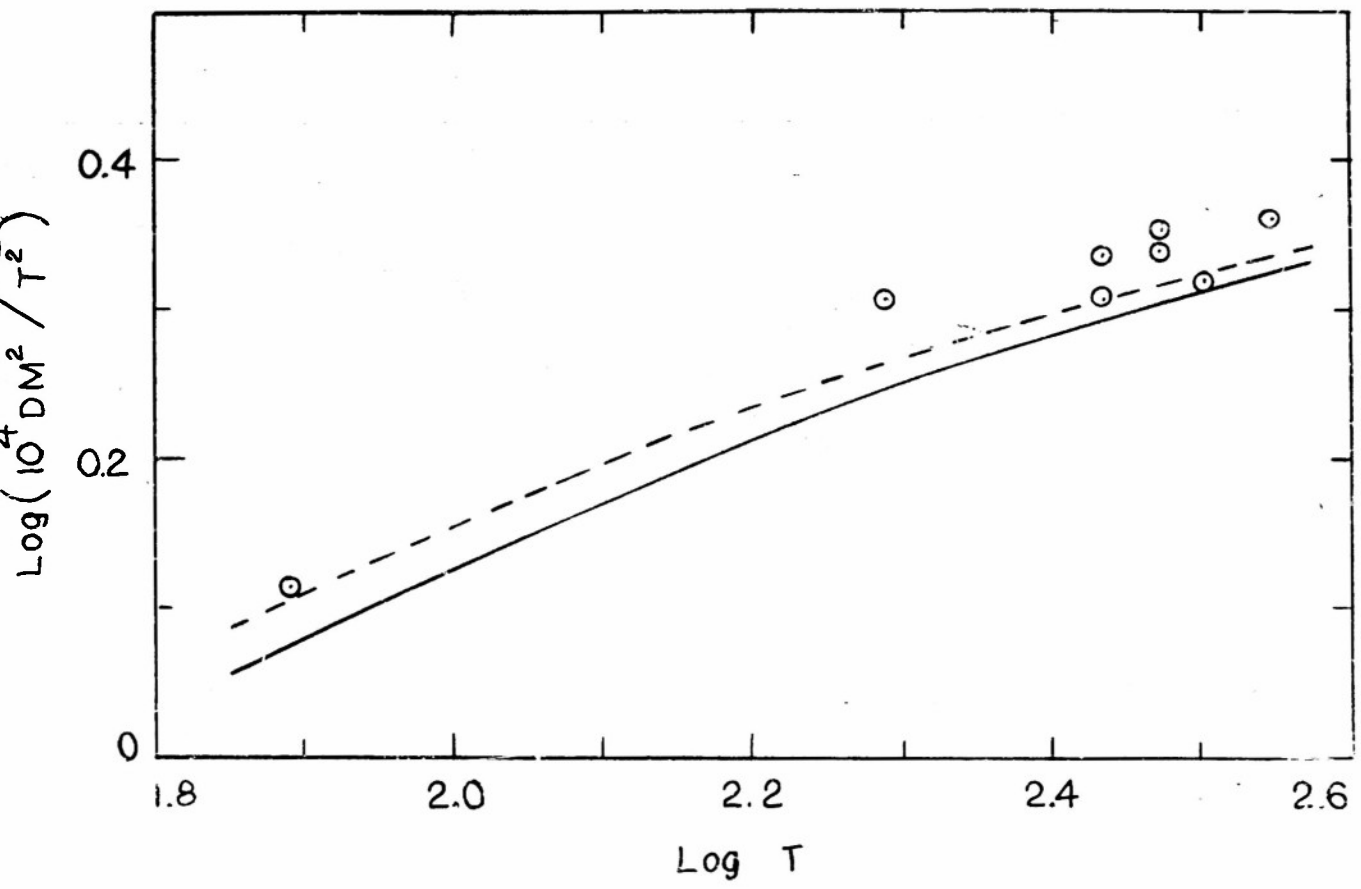

Fig. 8. Comparison of the observed self-diffusion coefficients of nitrogen with those calculated for the exp-six potential. Solid line: calculated using the parameters derived from crystal properties and second virial coefficients; broken line: calculated using the parameters derived from viscosity.

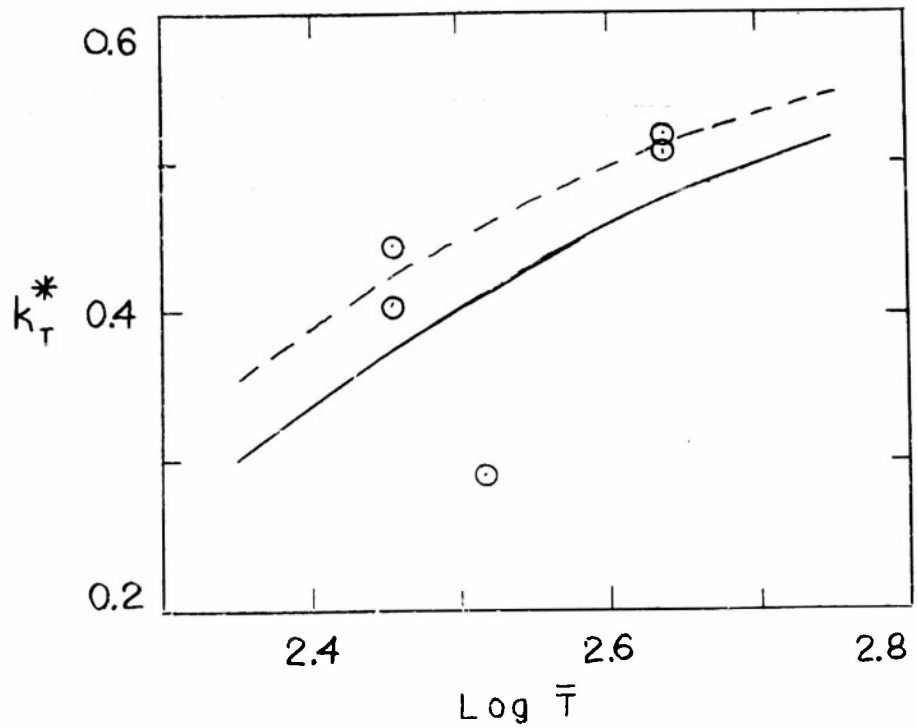

Fig. 9. Comparison of the observed reduced thermal diffusion ratios of nitrogen with those calculated for the exp-six potential. Solid line: calculated using the parameters derived from crystal properties and second virial coefficients; broken line: calculated using the parameters derived from viscosity.

calculated from the two sets of parameters for nitrogen. The parameters derived from the viscosity give better agreement than those derived from crystal and second virial coefficient data. Thus if it is necessary to calculate some property of a gas composed of non-spherical molecules, it is probably best to use parameters derived from equilibrium measurements if the desired property is an equilibrium one, and to use parameters derived from the viscosity for calculating transport properties.

SUMMARY

The three-parameter exp-six intermolecular potential has been shown to be able to predict, with a single set of potential parameters, the properties of gases composed of spherical molecules with fair accuracy. For the gases considered here, however, the simpler two-parameter L. J. (12-6) potential is scarcely inferior (in contrast to the case of helium and hydrogen[3]). For gases whose molecules deviate appreciably from spherical symmetry, a single set of potential parameters is not able to reproduce all the measured properties. Since the form of the exp-six potential is physically realistic and quite flexible, such behavior would seem to indicate that the assumptions of central intermolecular forces and elastic intermolecular collisions made in the basic theory are inadequate to describe the behavior of most real gases.

APPENDIX

The tabulations of transport property collision integrals and second virial coefficients given in references (1) and (2) for the exp-six potential extend from $\alpha = 12$ to 15. This range of the parameter α is sufficient for all spherical molecules so far investigated, but non-spherical molecules seem to require larger values of α. We have, therefore, extended the tabulations by extrapolation, with a consequent reduction in accuracy. Whereas the tabulations for $\alpha = 12$ to 15 were for the most part accurate to within a few tenths of one percent, the extrapolations may well involve uncertainties amounting to several percent.

The reduced second virial coefficients, $B^*(\alpha, T^*)$, defined by Eq. (4) were extrapolated graphically to $\alpha = 17$. The values of $B^*(\alpha, T^*)$ are nearly linear in $(\log \alpha)$, so that the extrapolation is simple. Values of $B^*(\alpha, T^*)$ are given in Table IV for $\alpha = 16, 17$.

Some of the reduced collision integrals, $\Omega^{(\ell, n)^*}(\alpha, T^*)$, two of which appear explicitly in Eqs. (7)-(9), were extrapolated to $\alpha = 16, 17$. These functions are nearly linear in α. The functions $\Omega^{(\ell, n)^*}$ are not tabulated directly, but instead the related functions,

$$Z^{(\ell, n)} = \left[T^*(1 - 6/\alpha)\right]^{\frac{1}{3}} \Omega^{(\ell, n)^*}, \qquad (12)$$

which are more suitable for interpolation purposes, are given in Table V.

TABLE IV

The reduced second virial coefficients.

T*	B*(α , T*)	
	α = 16	α = 17
.40	-8.60	-8.28
.45	-6.68	-6.44
.50	-5.40	-5.19
.60	-3.82	-3.67
.70	-2.88	-2.77
.80	-2.26	-2.16
.90	-1.83	-1.75
1.0	-1.505	-1.429
1.2	-1.063	-1.000
1.4	-0.772	-0.717
1.6	-0.568	-0.518
1.8	-0.420	-0.375
2.0	-0.302	-0.259
2.5	-0.107	-0.070
3.0	0.016	0.048
3.5	0.099	0.128
4.0	0.159	0.188
4.5	0.201	0.227
5	0.236	0.261
6	0.284	0.307
7	0.316	0.338
8	0.338	0.360
9	0.354	0.375
10	0.366	0.387
20	0.397	0.417
30	0.393	0.412
40	0.383	0.402
50	0.373	0.393
60	0.364	0.384
70	0.356	0.376
80	0.348	0.368
90	0.341	0.361
100	0.334	0.355

TABLE V

Collision integral functions.

T*	$\alpha = 16$				$\alpha = 17$			
	$Z^{(1, 1)}$	$Z^{(1, 2)}$	$Z^{(2, 2)}$	$Z^{(2, 3)}$	$Z^{(1, 1)}$	$Z^{(1, 2)}$	$Z^{(2, 2)}$	$Z^{(2, 3)}$
0	1.187	1.055	1.195	1.095	1.187	1.055	1.195	1.095
.1	1.167	1.029	1.197	1.099	1.160	1.025	1.190	1.092
.2	1.153	1.012	1.204	1.107	1.148	1.010	1.196	1.100
.3	1.[illegible]	0.977	1.207	1.105	1.125	0.977	1.201	1.102
.4	1.[illegible]	0.937	1.198	1.082	1.099	0.943	1.196	1.084
.5	1.070	0.903	1.178	1.051	1.074	0.912	1.180	1.058
.6	1.043	0.876	1.154	1.021	1.050	0.888	1.159	1.031
.7	1.[illegible]	0.856	1.130	0.995	1.029	0.871	1.138	1.007
.8	1.[illegible]	0.841	1.108	0.974	1.012	0.858	1.119	0.988
.9	0.[illegible]	0.831	1.088	0.958	0.998	0.849	1.101	0.974
1.0	0.971	0.824	1.072	0.946	0.987	0.844	1.087	0.963
1.2	0.952	0.818	1.048	0.931	0.971	0.839	1.065	0.950
1.4	0.941	0.817	1.032	0.925	0.962	0.840	1.052	0.946
1.6	0.[illegible]	0.820	1.023	0.925	0.957	0.844	1.044	0.947
1.8	0.932	0.825	1.019	0.928	0.956	0.850	1.041	0.951
2.0	0.932	0.831	1.017	0.933	0.957	0.858	1.041	0.958
2.5	0.[illegible]	0.849	1.023	0.951	0.966	0.878	1.050	0.978
3.0	0.949	0.867	1.036	0.972	0.979	0.899	1.065	1.002
3.5	0.962	0.886	1.052	0.993	0.994	0.920	1.083	1.025
4	0.975	0.903	1.069	1.014	1.010	0.940	1.102	1.048
5	1.002	0.936	1.103	1.053	1.041	0.976	1.139	1.090
6	1.[illegible]	0.964	1.135	1.088	1.070	1.007	1.175	1.129
7	1.[illegible]	0.990	1.165	1.119	1.097	1.036	1.208	1.163
8	1.[illegible]	1.013	1.193	1.147	1.122	1.061	1.238	1.194
9	1.[illegible]	1.034	1.219	1.172	1.145	1.085	1.266	1.221
10	1.115	1.053	1.242	1.195	1.167	1.106	1.292	1.247
12	1.[illegible]	1.086	1.284	1.236	1.205	1.144	1.339	1.292
14	1.[illegible]	1.115	1.321	1.272	1.239	1.177	1.379	1.331
16	1.[illegible]	1.142	1.354	1.304	1.270	1.207	1.415	1.366
18	1.[illegible]	1.165	1.384	1.332	1.298	1.233	1.448	1.398
20	1.[illegible]	1.186	1.411	1.358	1.323	1.258	1.478	1.426
25	1.[illegible]	1.233	1.470	1.415	1.379	1.311	1.543	1.489
30	1.[illegible]	1.273	1.520	1.463	1.427	1.357	1.598	1.542
35	1.[illegible]	1.307	1.564	1.506	1.468	1.397	1.647	1.589
40	1.[illegible]	1.339	1.603	1.544	1.506	1.434	1.689	1.630
45	1.[illegible]	1.367	1.639	1.578	1.540	1.466	1.728	1.668
50	1.[illegible]	1.393	1.671	1.610	1.571	1.497	1.764	1.703
60	1.[illegible]	1.440	1.730	1.668	1.627	1.552	1.828	1.766
70	1.[illegible]	1.482	1.782	1.719	1.677	1.601	1.885	1.822
80	1.[illegible]	1.520	1.828	1.765	1.722	1.645	1.936	1.873
90	1.[illegible]	1.554	1.871	1.807	1.763	1.685	1.983	1.919
100	1.[illegible]	1.587	1.910	1.847	1.801	1.723	2.026	1.962

In Table VI are given the values of the following ratios of collision integrals which occur frequently:

$$A^* = \Omega^{(2,2)^*} / \Omega^{(1,1)^*}, \qquad (13)$$

$$C^* = \Omega^{(1,2)^*} / \Omega^{(1,1)^*}.$$

Table VI also gives the values of the first approximation to the reduced thermal diffusion ratio, $\left[k_T^*\right]_1$, as calculated from a simple, accurate formula derived by Kihara[17]:

$$\left[k_T^*\right]_1 = \frac{15}{16}\,\frac{(6C^* - 5)}{A^*}. \qquad (14)$$

This expression gives values of k_T^* which differ from the values calculated from the elaborate expressions for $\left[k_T^*\right]_2$ in reference (1) by no more than the uncertainties involved in the extrapolations of the $\Omega^{(\ell,\,n)^*}$.

The quantities $f^{(m)}(\alpha, T^*)$ which appear in Eqs. (7)-(9) are functions of the reduced collision integrals, $\Omega^{(\ell,\,n)^*}$, and are used for calculating higher approximations to the transport coefficients. The superscript indicates the order of approximation used in computing these functions. Kihara[17] has given simple expressions for these functions which differ from the more elaborate expressions used in reference (1) by less than the uncertainty involved in the extrapolations of the $\Omega^{(\ell,\,n)^*}$. The values of the f's were therefore calculated according to Kihara's expressions:

$$f_\eta^{(2)} = 1 + \frac{3}{49}\left[\frac{4\Omega^{(2,3)^*}}{\Omega^{(2,2)^*}} - \frac{7}{2}\right]^2,$$

$$f_\lambda^{(2)} = 1 + \frac{2}{21}\left[\frac{4\Omega^{(2,3)^*}}{\Omega^{(2,2)^*}} - \frac{7}{2}\right]^2, \qquad (15)$$

$$f_D^{(2)} = 1 + \frac{(6C^* - 5)^2}{16A^* + 40},$$

and are tabulated in Table VII.

(17) T. Kihara, Imperfect Gases, originally published in Japanese (Asakusa Bookstore, Tokyo, 1949) and translated into English by the U. S. Office of Air Research, Wright-Patterson Air Force Base.

TABLE VI

The functions A* , C* , and the reduced thermal diffusion ratio, $\left[k_T^*\right]_1$.

T*	$\alpha = 16$			$\alpha = 17$		
	A*	C*	$\left[k_T^*\right]_1$	A*	C*	$\left[k_T^*\right]_1$
0	1.006	0.889	0.311	1.006	0.889	0.311
.1	1.031	0.886	0.286	1.036	0.886	0.287
.2	1.047	0.880	0.251	1.050	0.882	0.262
.3	1.070	0.866	0.170	1.070	0.870	0.193
.4	1.089	0.852	0.097	1.088	0.858	0.127
.5	1.101	0.844	0.052	1.099	0.850	0.084
.6	1.107	0.840	0.034	1.104	0.846	0.066
.7	1.108	0.840	0.032	1.106	0.846	0.064
.8	1.108	0.842	0.042	1.105	0.848	0.074
.9	1.106	0.845	0.060	1.104	0.851	0.091
1.0	1.104	0.849	0.081	1.102	0.855	0.111
1.2	1.100	0.859	0.130	1.097	0.864	0.158
1.4	1.097	0.868	0.179	1.093	0.873	0.206
1.6	1.094	0.877	0.223	1.091	0.882	0.249
1.8	1.093	0.885	0.263	1.089	0.889	0.289
2.0	1.092	0.891	0.299	1.088	0.896	0.323
2.5	1.091	0.905	0.368	1.087	0.909	0.391
3.0	1.092	0.914	0.417	1.087	0.918	0.439
3.5	1.094	0.921	0.453	1.089	0.925	0.475
4	1.096	0.927	0.478	1.091	0.930	0.500
5	1.100	0.934	0.513	1.095	0.937	0.534
6	1.104	0.938	0.531	1.098	0.941	0.553
7	1.107	0.940	0.544	1.101	0.944	0.566
8	1.110	0.942	0.550	1.104	0.946	0.572
9	1.112	0.944	0.557	1.106	0.947	0.580
10	1.114	0.944	0.560	1.108	0.948	0.582
12	1.118	0.945	0.564	1.111	0.949	0.588
14	1.120	0.946	0.563	1.113	0.950	0.587
16	1.122	0.946	0.564	1.114	0.950	0.590
18	1.124	0.946	0.564	1.116	0.950	0.589
20	1.125	0.946	0.564	1.117	0.951	0.591
25	1.128	0.946	0.563	1.119	0.951	0.591
30	1.131	0.946	0.563	1.120	0.951	0.591
35	1.133	0.947	0.564	1.121	0.952	0.593
40	1.134	0.947	0.564	1.121	0.952	0.595
45	1.136	0.947	0.564	1.122	0.952	0.596
50	1.137	0.948	0.567	1.123	0.953	0.598
60	1.139	0.949	0.569	1.124	0.954	0.602
70	1.141	0.949	0.572	1.124	0.954	0.605
80	1.143	0.950	0.574	1.124	0.955	0.609
90	1.145	0.951	0.578	1.125	0.956	0.613
100	1.146	0.952	0.582	1.125	0.957	0.618

TABLE VII

Functions for calculating higher approximations to the transport coefficients.

T*	$\alpha = 16$			$\alpha = 17$		
	$f_\eta^{(2)}$	$f_\lambda^{(2)}$	$f_D^{(2)}$	$f_\eta^{(2)}$	$f_\lambda^{(2)}$	$f_D^{(2)}$
0	1.0017	1.0026	1.0020	1.0017	1.0026	1.0020
.1	1.0018	1.0028	1.0018	1.0018	1.0028	1.0018
.2	1.0020	1.0031	1.0014	1.0020	1.0030	1.0015
.3	1.0016	1.0025	1.0007	1.0017	1.0027	1.0009
.4	1.0008	1.0012	1.0002	1.0010	1.0016	1.0004
.5	1.0003	1.0005	1.0001	1.0005	1.0007	1.0002
.6	1.0001	1.0001	1.0000	1.0002	1.0003	1.0001
.7	1.0000	1.0000	1.0000	1.0001	1.0002	1.0001
.8	1.0000	1.0000	1.0000	1.0001	1.0001	1.0001
.9	1.0000	1.0000	1.0001	1.0001	1.0001	1.0002
1.0	1.0001	1.0001	1.0002	1.0001	1.0002	1.0003
1.2	1.0002	1.0003	1.0004	1.0003	1.0005	1.0006
1.4	1.0004	1.0007	1.0008	1.0006	1.0009	1.0010
1.6	1.0008	1.0013	1.0012	1.0010	1.0016	1.0015
1.8	1.0013	1.0019	1.0016	1.0015	1.0023	1.0020
2.0	1.0017	1.0027	1.0021	1.0020	1.0030	1.0024
2.5	1.0029	1.0045	1.0032	1.0032	1.0049	1.0036
3.0	1.0039	1.0060	1.0041	1.0042	1.0065	1.0045
3.5	1.0047	1.0073	1.0049	1.0051	1.0079	1.0053
4	1.0054	1.0083	1.0054	1.0057	1.0089	1.0059
5	1.0062	1.0096	1.0063	1.0066	1.0103	1.0068
6	1.0067	1.0105	1.0068	1.0072	1.0111	1.0073
7	1.0071	1.0110	1.0072	1.0075	1.0117	1.0077
8	1.0073	1.0113	1.0073	1.0077	1.0120	1.0079
9	1.0074	1.0115	1.0076	1.0078	1.0122	1.0081
10	1.0074	1.0116	1.0077	1.0079	1.0123	1.0082
12	1.0075	1.0117	1.0078	1.0080	1.0124	1.0084
14	1.0075	1.0117	1.0078	1.0080	1.0124	1.0084
16	1.0075	1.0117	1.0079	1.0080	1.0124	1.0085
18	1.0075	1.0117	1.0079	1.0080	1.0124	1.0085
20	1.0075	1.0117	1.0079	1.0079	1.0123	1.0086
25	1.0075	1.0117	1.0079	1.0079	1.0123	1.0086
30	1.0075	1.0117	1.0079	1.0079	1.0123	1.0086
35	1.0076	1.0117	1.0080	1.0079	1.0123	1.0087
40	1.0076	1.0118	1.0080	1.0080	1.0124	1.0087
45	1.0076	1.0119	1.0080	1.0080	1.0124	1.0088
50	1.0077	1.0119	1.0081	1.0080	1.0124	1.0088
60	1.0078	1.0121	1.0082	1.0081	1.0126	1.0090
70	1.0079	1.0123	1.0083	1.0082	1.0128	1.0091
80	1.0081	1.0125	1.0084	1.0083	1.0130	1.0092
90	1.0081	1.0126	1.0085	1.0084	1.0131	1.0093
100	1.0082	1.0128	1.0087	1.0085	1.0133	1.0095